

Flash photolysis and time-resolved electron spin resonance studies of triplet benzophenone quenching by hindered amine light stabilizers (HALS). A comparison of HALS amines and aminoethers as electron and hydrogen atom donors

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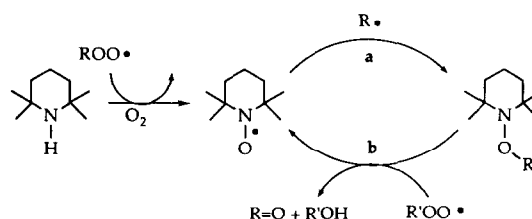
Abstract

Transient absorption spectroscopy and time-resolved electron spin resonance (TR-ESR) were employed to understand the electron and hydrogen atom transfer quenching of triplet benzophenone (³BP) in acetonitrile and benzene by amine and aminoether derivatives of 2,2,6,6-tetramethylpiperidine (hindered amine light stabilizers, HALS). The amines (I and II) are efficient quenchers of ³BP. The observed quenching rate constants were found to be in the range 6×10^8 – 6×10^9 M⁻¹ s⁻¹ and depend on the structure of the amine and the solvent. On the other hand, the aminoethers (III and IV) do not exhibit any quenching at all. Reactions of ³BP with amines I and II in benzene yield ketyl radicals (detected by transient absorption spectroscopy) and the corresponding aminyl or aminomethyl radicals (detected by TR-ESR). Neither experimental method provided any evidence for products of the reactions of ³BP with aminoethers III and IV. The experimental results are discussed from the viewpoint of the mechanism of polymer stabilization by HALS.

1. Introduction

The class of compounds called hindered amine light stabilizers (HALS), amine and aminoether derivatives of 2,2,6,6-tetramethylpiperidine, are recognized as very efficient polymer light stabilizers [1–5]. Although HALS have been widely studied within the last 20 years, several aspects of their activity are far from completely understood [6–8].

Chemical scavenging of alkyl and peroxy macroradicals is considered to be the most important process in the mechanism of polymer stabilization by HALS [6]. It is commonly accepted that during polymer exposure, both amine and aminoether derivatives of HALS yield nitroxides which function as interceptors of alkyl radicals to yield aminoethers. These aminoethers in turn react with peroxy radicals to regenerate nitroxides. Therefore the interconversions of HALS of various structures operate in a cyclic pathway as depicted in Scheme 1.



Scheme 1.

Reaction step **a** in this cycle is known to proceed at a high rate, *i.e.* the rate constants of nitroxide scavenging of different carbon-centered radicals are 10^7 – 10^9 M⁻¹ s⁻¹ in non-viscous homogeneous solution [9]. In polymer media this reaction is probably controlled by molecular diffusion. Peroxy radicals are known to be less reactive with nitroxides [10] and therefore nitroxide scavenging of peroxy radicals is not considered to be an important reaction in the stabilization by HALS.

Reaction step **b** is not well studied [6–8, 11, 12]. It has been proposed that reactions of peroxy radicals with HALS aminoethers yield nitroxides along with peroxides, although until recently [6,

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12] no mechanistic studies have been reported. In the latter papers, reaction of peroxy radicals of various structures (both alkyl and acyl) with HALS aminoethers in chlorobenzene at 60 °C was shown to yield nitroxides, ketones, alcohols and carboxylic acids, depending on the structure of the peroxy radical. By employing isotopic labeling (oxygen-18), the label was found to incorporate into the nitroxide and alcohol formed from the alkyl peroxy radicals, but not into the ketone formed from the aminoether (Scheme 1). On the basis of these results, the authors [6, 12] suggested that the regeneration of the nitroxide in the reaction of peroxy radicals with HALS aminoether proceeded through a charge transfer mechanism involving primary electron transfer from an aminoether to an alkyl- or acylperoxy radical.

The properties of peroxy radicals as electron acceptors depend crucially on the solvent, *i.e.* they are very weak acceptors in non-polar organic solvents [13, 14b] and much more powerful in aqueous solutions [14, 15]. It has also been found that the rate constants for the reduction of substituted methylperoxy radicals by an ascorbate ion and tetramethylene-*p*-phenylenediamine increased as the electron-withdrawing capacity of the substituents in the peroxy radicals increased and could approach values of 10^8 – 10^9 M⁻¹ s⁻¹ [14a]. In non-polar organic media, however, the rate constants of electron transfer to peroxy radicals from electron donors should be orders of magnitude less and should compete with the more common reaction of hydrogen abstraction.

For HALS amines and aminoethers, which do not donate electrons as well as the ascorbate ion or tetramethylene-*p*-phenylenediamine, determination of the rate of electron transfer to peroxy radicals in non-polar organic media (which mimics the polarity of a polymer environment) is expected to be more difficult. HALS amines should possess the same electron donor properties as typical aliphatic amines, although, to the best of our knowledge, there are no quantitative reports concerning the electron donor properties of aminoethers. To check for the possibility of electron transfer from HALS aminoethers to peroxy radicals, which are known to be weak electron acceptors in organic media, we decided to investigate an extreme case as a model, and to use triplet benzophenone as an electron acceptor and to compare the results with HALS amines and aminoethers serving as electron donors.

Owing to its electrophilic character, the $n\pi^*$ triplet state of benzophenone is a powerful one-electron oxidant [16] and acts as an acceptor of

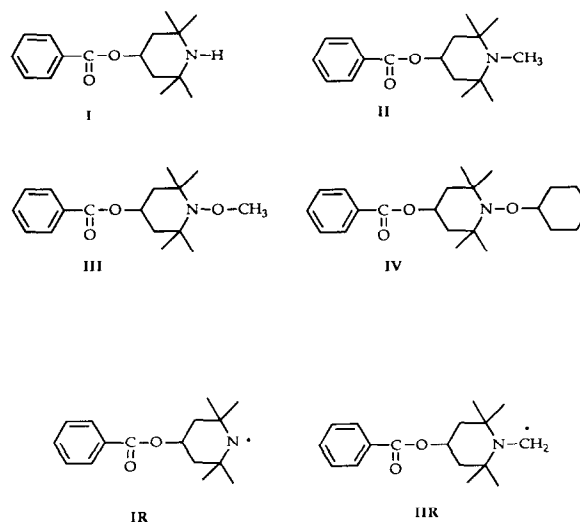


Chart 1.

both electrons and hydrogen atoms. The reactions of triplet excited benzophenone with different amines have been studied by transient absorption spectroscopy on the micro- to femtosecond time scale (see ref. 17 for reviews). The detailed mechanism of the reaction depends on the exact properties of the amine and the polarity of the solvent, although it commonly includes a primary stage of the formation of a triplet charge transfer complex (CTC), followed by hydrogen atom transfer resulting in the formation of a ketyl radical of benzophenone and an aminyl or alkyl radical of an amine [17].

In this investigation we determined the relative efficiencies for the quenching of the excited triplet state of benzophenone by two HALS amines (I and II, see Chart 1) and by two aminoethers (III and IV, see Chart 1). By transient absorption spectroscopy, we monitored the primary radicals formed in the same reaction by time-resolved electron spin resonance (TR-ESR).

2. Experimental details

HALS compounds (I–IV, see Chart 1) were obtained from Ciba-Geigy; benzophenone (Aldrich Gold Label), benzene (Aldrich, spectrograde) and acetonitrile (Fischer, HPLC) were used as received.

Flash photolysis experiments were performed at room temperature using a Lambda Physic excimer laser ($\lambda = 308$ nm, $\tau = 15$ ns) for excitation, employing a set-up described previously [18]. Solutions of benzophenone (5.5 mM) in benzene or acetonitrile with varying concentrations of I–IV (0.3–20

mM) were bubbled with Ar prior to the measurements.

TR-ESR spectra were recorded on a system that has been described previously [19], employing a Bruker ER 100D ESR instrument with a broad band preamplifier, a Quanta Ray Nd:YAG laser ($\lambda=355$ nm, $\tau=10$ ns) and an EG&G PARC boxcar yielding a response time of about 200 ns. An argon-flushed solution was passed through a flat quartz cell at a rate of 0.7–1 ml min⁻¹.

3. Results

3.1. Transient absorption measurements

In benzene and acetonitrile and in the absence of electron or hydrogen atom donors, the spectrum corresponds to a benzophenone (BP) triplet (³BP) immediately after the flash, with maximum absorption around 530 nm [17]. No long-lived transients were observed. Similar spectra were observed immediately after the flash in the presence of I and II (see Chart 1); however, addition of amine I or II shortens the triplet lifetime and leads to the production of long-lived ketyl radicals of BP (BPH), which also absorb near 530 nm [17, 20]. The kinetics of the decay of transient absorption of those solutions containing BP and I or II in benzene (or acetonitrile) at 530 nm are shown in Fig. 1(a). Fast decay at early time corresponds to ³BP and slow decay at later time corresponds to BPH. The rate constants of ³BP quenching (k_q) by I and II were determined from the dependence of the effective pseudo-first-order triplet decay rate constants on the concentration of amine, [C], via

$$k_{\text{eff}} = k_0 + k_q[C] \quad (1)$$

where k_{eff} and k_0 are the decay rate constants of ³BP with quencher of concentration [C] and without quencher respectively. Figure 2 presents the data for ³BP quenching experiments by I and II in benzene and acetonitrile plotted according to eqn. (1); Table 1 summarizes the corresponding quenching rate constants k_q .

The yield of BPH from ³BP is proportional to the ratio $r = \Delta D_{\text{R}}^{\infty} / \Delta D_{\text{T}}^0$, where ΔD_{T}^0 and $\Delta D_{\text{R}}^{\infty}$ are the transient absorbances corresponding to the initial formation of the triplet immediately after the flash and to the formation of the ketyl radical respectively. Since the lifetime of BPH is much greater than that of triplet BP, $\Delta D_{\text{R}}^{\infty}$ may be found by an extrapolation of the ketyl radical decay curve back to zero time [20]. For II the relative quantum yield of BPH formation in both solvents is approximately twice as large as for I.

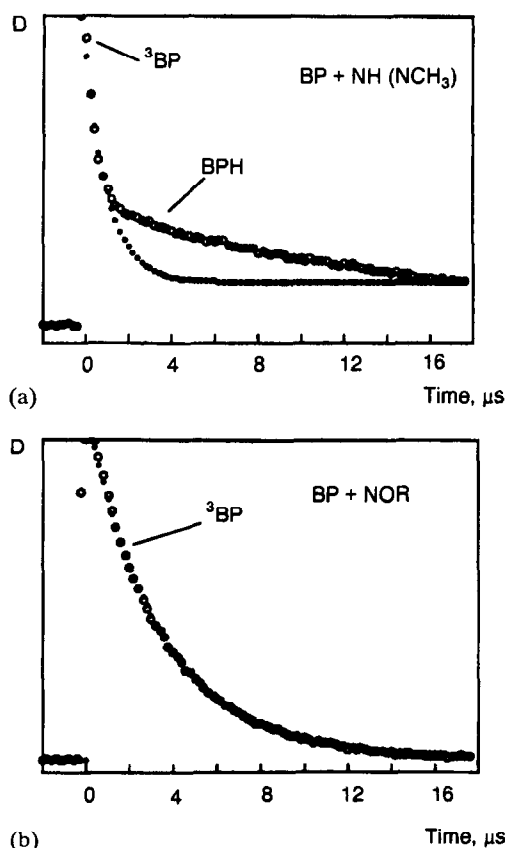


Fig. 1. Decay of transient absorption at 530 nm following laser flash photolysis at 308 nm of solutions of benzophenone (BP) in benzene with HALS amines I and II (a) and aminoethers III and IV (b).

In contrast with the results with amines as quenchers, addition of aminoethers III and IV (see Chart 1) to a benzene or acetonitrile solution of BP does not result in the formation of BPH (see Fig. 1(b)). Transient spectra of BP taken immediately after the flash with III or IV are the same as with I or II or without any quencher and have a maximum around 530 nm, which corresponds to ³BP. However, within the concentration range of III and IV of about 0.3–15 mM in both benzene and acetonitrile there is no quenching of ³BP.

3.2. Time-resolved ESR experiments

Photolysis of benzene solutions of BP (0.1 M) containing I or II yields intense electron polarization spectra of the radicals (Figs. 3 and 4).

TR-ESR spectra of BP solutions containing I (0.03 M) (Fig. 3) are interpreted as a superimposition of two individual spectra: the spectrum of the ketyl radical BPH, which appears as a broad singlet in the center of the spectrum with indi-

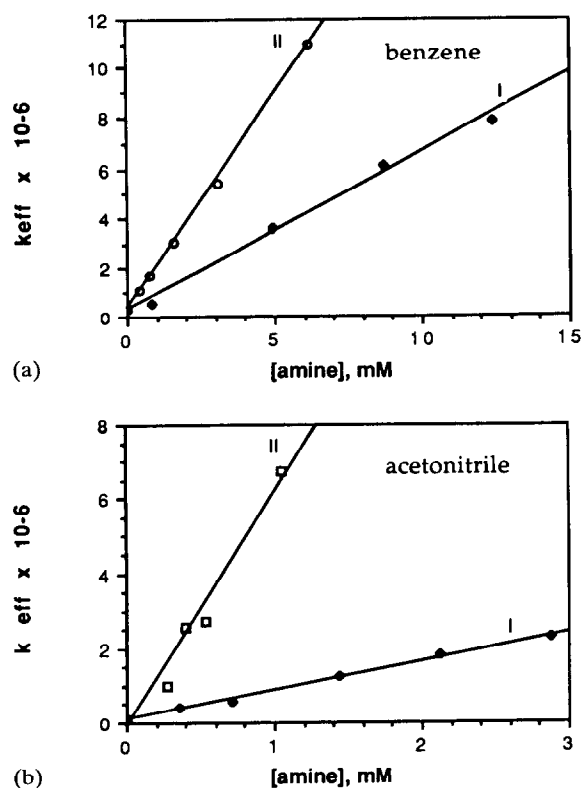


Fig. 2. Effective first-order decay constants of triplet benzophenone (^3BP) vs. amine (I and II) concentration in benzene (a) and acetonitrile (b).

TABLE 1. Rate constants for quenching of excited triplet state of benzophenone (^3BP) by HALS amines I and II in benzene and acetonitrile

Donor	k_q ($\text{M}^{-1} \text{s}^{-1}$)	
	Benzene	Acetonitrile
I	6.3×10^8	7.7×10^8
II	1.7×10^9	6.2×10^9

cations of hyperfine splitting (Fig. 3(b)), is superimposed on the spectrum of a triplet, which has been assigned to the radical IR (Chart 1). Line separations of the proposed triplet in Fig. 3 are consistent with literature hyperfine coupling (HFC) constants for an odd electron on a ^{14}N nucleus (14.6 G) [21]. The large width of each of the three lines of the aminyl radical spectra is assigned to unresolved HFC with 12 protons of four methyl groups [21a]. In the presence of oxygen the central and left lines in the spectra split into two peaks at early time, whereas at later time the original lines disappear and only the new sharp peaks appear, which are shifted about 3.5 G downfield (see Figs. 3(c) and 3(d)). We ascribed the three line spectra observed at later time in the

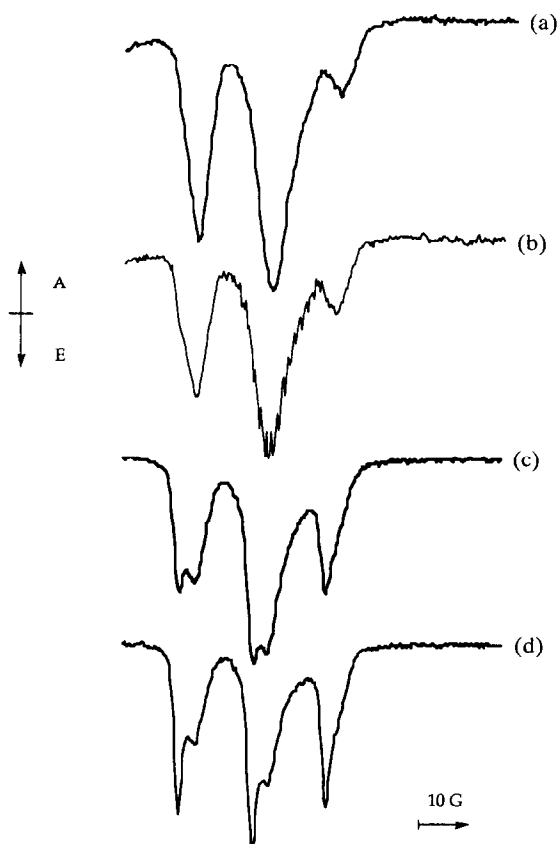
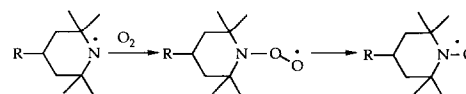


Fig. 3. Time-resolved ESR spectra observed on photolysis of benzophenone (BP) with amine I (0.03 M) in benzene 100–400 ns (a) and 700–1000 ns (b) after laser flash; (c) and (d) are the corresponding spectra in the presence of a small amount of oxygen.

presence of oxygen to nitroxide, which we propose is formed according to the following reactions [22]:



It is known that nitroxides have larger g factors than the relative aminyl radicals, with the difference being about 0.0015–0.002 [21, 22]. The experimental nitroxide spectra observed at later times are shifted vs. the aminyl spectra by about 3.5 G downfield, which one may expect from the difference in g factors between the aminyl radical and a nitroxide.

Although several mechanisms have been proposed for the conversion of N -peroxy radical (which has been observed experimentally by ESR [22a, b]) into nitroxide, none of them has been confirmed experimentally [22]. Therefore we employ a minimum reaction scheme and display only the species which have been detected experimentally.

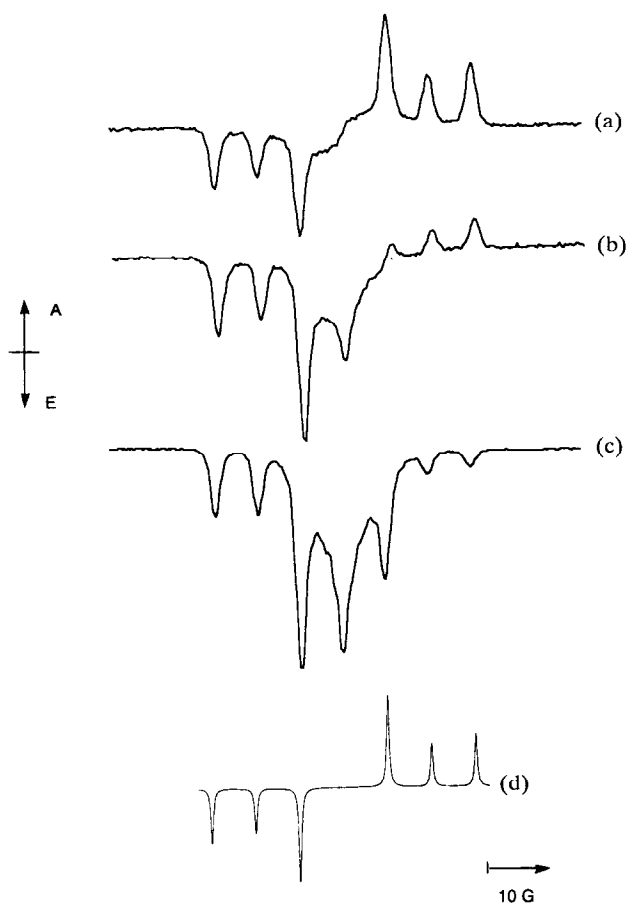


Fig. 4. Time-resolved ESR spectra observed on photolysis of benzophenone (BP) with amine **II** at various concentrations in benzene 100–400 ns after laser flash: 0.01 M (a), 0.05 M (b) and 0.2 M (c); simulated spectra (d).

The polarization pattern of the spectra is not changed with the concentration of **I** within the range 0.01–0.2 M (but there is a significant increase in the spectral intensity). Taking into account the ^3BP quenching rate constant determined by flash photolysis ($6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and the employed concentration range of **I**, the effective pseudo-first-order rate constant of ^3BP quenching by **I** changes from 6.3×10^6 to $1.3 \times 10^8 \text{ s}^{-1}$. The rate of spin–lattice relaxation in the triplet state of ketones in solution is considered to be of the order 10^8 – 10^9 s^{-1} [23], e.g. for xanthone it was measured to be $1.8 \times 10^8 \text{ s}^{-1}$ [24]. Thus the absence of changes in the polarization pattern of the BP–**I** system in benzene within the employed concentrations means that the quenching of ^3BP by **I** cannot compete with spin relaxation and therefore the triplet (T) (see ref. 25 for reviews) mechanism cannot be responsible for the observed polarization.

The different intensities of low and high field components of the observed spectra of aminyl

radicals are probably a result of the simultaneous operation of both the radical pair (RP) mechanism [25], which gives emission–absorption (E–A) spectra, and the triplet–radical pair (TRP) mechanism [26], which gives pure emission (E) spectra. Polarization according to the RP mechanism is probably formed during the recombination of aminyl radicals, while the TRP mechanism operates in ^3BP –aminyl radical pairs. The emissively polarized nitroxide formed from the aminyl radical in the presence of oxygen exhibits polarization according to the TRP mechanism in a similar way [26b].

Thus, the data in Fig. 3 indicate that an aminyl radical **IR** is formed in addition to a ketyl radical under BP photolysis in benzene in the presence of **I**. However, no polarization is observed under similar conditions for the photolysis of the BP–**I** system in acetonitrile.

The TR-ESR spectra observed for the photolysis of BP in the presence of **II** in benzene are dependent on the concentration of the donor (Figs. 4(a)–4(c)). In addition to BPH, an expected radical is formed in this system, **IIR** (Chart 1). To the best of our knowledge, no ESR spectra of this radical are available in the literature; however, a few examples of radicals with an N–CH₂ radical center with two aliphatic hydrocarbon substituents at the nitrogen atom are known [27]. They all have HFC constants of about 7 G for coupling to nitrogen (a_N) and about 13–14 G for coupling to α -hydrogen (a_H). On the basis of these values, the stick diagram of the ESR spectrum which one may expect from **IIR** is expected to have a seven-line pattern with 1:1:3:2:3:1:1 intensities. The TR-ESR spectrum shown in Fig. 4(a) observed under a low (0.01 M) concentration of **II** is close to the expected pattern, except that the central line is absent owing to phase alteration [25]. Experimental values from the spectrum are $a_N = 7.1 \text{ G}$ and $a_H \approx 14.2 \text{ G}$. The relatively clean E–A polarization of the spectrum in Fig. 4(a) is formed nearly exclusively by an RP mechanism during the decay of **IIR** radicals. The spectra obtained for **IIR** are polarized according to the RP mechanism and were simulated employing the HFC constants given above (Fig. 4(d)). At a high concentration (0.2 M) of the donor the experimental spectra (Fig. 4(c)) are a superimposition of emissively (E) polarized **IIR** and E-polarized spectra of BPH (broad singlet in the center). The line intensities in the spectra are probably distorted because of the contribution of the RP mechanism (see Fig. 4(a)). At a concentration of **II** of about 0.2 M the effective decay of ^3BP is about $3.4 \times 10^8 \text{ s}^{-1}$. This decay is not fast enough to compete favorably with the

process of spin–lattice relaxation in polarized ^3BP [23, 24] and as a result allows the observation of the polarization formed in the reaction via the triplet (T) mechanism [25]. However, for concentrations of **II** of about 0.01 M the spin–lattice relaxation of ^3BP is much faster than the reaction and no net polarization is observed. The spectra recorded at a concentration of about 0.05 M **II** (Fig. 4(b)) show evidence of a mixed mechanism of polarization.

Therefore the experimental results of BP photolysis with **II** confirm the formation of **IIR** along with BPH during benzophenone photoreduction. However, no polarization is observed during photolysis of BP–**II** in acetonitrile.

Photolysis of BP in benzene or acetonitrile in the presence of **III** or **IV** did not produce measurable polarization.

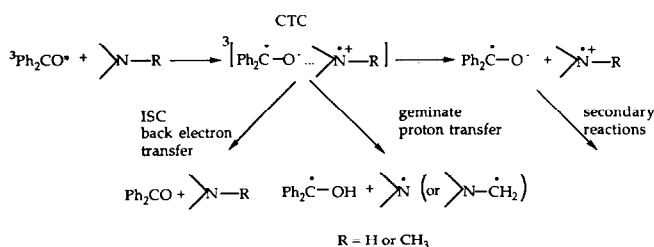
4. Discussion

On the basis of the experimental results of both transient absorption and TR-ESR, we propose that HALS amines **I** and **II** react with ^3BP according to a mechanism similar to other aliphatic amines (Scheme 2) [20]. The initial step in this mechanism is the formation of a triplet excited charge transfer complex (^3CTC). The partial positive charge on the amine enhances the hydrogen atom transfer to form a ketyl radical of BP (BPH) and an aminomethyl (in the case of **II**) or an aminyl (in the case of **I**) radical. That the primary step of the reaction of ^3BP with amines involves a charge transfer step is consistent with the linear dependence found between $\log k_q$ and the ionization potential (IP) of amines [28]. Our experimental data support a CT mechanism for the quenching of BP by **I** and **II**. The ^3BP quenching rate constant (k_q) for **II** is larger than that for **I**, as expected, based on the IPs for 2,2,6,6-tetramethylpiperidine (8.04 eV) and *N*-methyl-2,2,6,6-tetramethylpiperidine (7.68 eV) [29]. The experimental values of k_q for both **I** and **II** are larger in acetonitrile than in benzene, which one would expect from the

stabilization of CTC in polar media, resulting in a larger rate of quenching of ^3BP by amines in polar media.

The TR-ESR results only report on the formation of radicals through hydrogen atom transfer, which is a “secondary” process in the course of the reaction of ^3BP with **I** and **II**. However, the reaction with **II** in benzene is fast enough at sufficiently high donor concentration (0.2 M) to compete with the spin–lattice relaxation of ^3BP . Under these conditions the initial polarization of triplet sub-levels is conserved and is transferred to the products, ketyl and aminomethyl radicals (see Fig. 4). The reaction of ^3BP with **I** in benzene is too slow to compete with spin relaxation even at the highest concentration of donor used (0.2 M) and no triplet polarization is observed in the formed radicals.

The absence of polarization in acetonitrile provides important information about the mechanism of the reaction of photoreduction of BP by **I** and **II**. From time-resolved optical measurements, ketyl radicals are formed in acetonitrile with a yield which is almost the same as that in benzene. If we assume the same yield for counter-radicals, this result means that the radicals formed during ^3BP photoreduction by **I** and **II** in acetonitrile either lose their polarization according to an unrecognized mechanism during the reaction in geminate pairs or are formed in some secondary reactions. Acetonitrile, being a polar solvent, stabilizes CTC and at the same time the high dielectric constant of the solvent eliminates the importance of coulombic interaction that keeps the charged species (anion radical of BP (BP^-) and aminyl cation radical (AM^+)) and CTC together for a significant period of time. In benzene, where the dielectric constant is low and coulombic interaction is significant, proton transfer takes place within CTC, and if the latter process is fast enough, the formed radicals (ketyl and aminoalkyl or aminyl) conserve the spin polarization of ^3BP , which is observed experimentally under high concentrations of **II**. In polar media the radical ions formed after primary electron transfer in the ^3BP –amine system are separated by solvent molecules and hydrogen atom transfer takes place at a rate which is slow enough to compete with spin–lattice relaxation. In addition, hydrogen atom transfer in free (diffusion) ion radical pairs and/or the degenerate electron exchange of BP^- and AM^+ with the corresponding neutral species are also possible and could quench the polarization. Such processes have been postulated in time-resolved chemical induced dynamic nuclear polarization (CIDNP) and stimulated nuclear polarization (SNP) ex-



Scheme 2.

periments with the anthraquinone–triethylamine system [30] and in chemical induced dynamic electron polarization (CIDEP) experiments with the BP–diethylaniline system [31]. Time-resolved magnetic resonance experiments are valuable complements to pico- and femtosecond laser flash photolysis studies of BP–amine systems [17c, d]. Steady state CIDNP has already been used for investigating the mechanism of BP–amine photoreactions [32] and the observed broadening of the resonance signals during photolysis in acetonitrile was ascribed to the degenerate electron exchange reactions [32b].

As mentioned above, neither **III** nor **IV** quenches ^3BP and photolysis of their solutions containing BP does not exhibit any CIDEP spectra in the reaction with ^3BP . The absence of ^3BP quenching by aminoethers means that there is no reaction and no significant CTC between these species. This result is understandable if the IP of aminoethers is much larger than that of amines and if the oxidation potential of ^3BP is not enough to induce electron transfer. Since **III** and **IV** do not have labile hydrogen to abstract, there is no measurable interaction between ^3BP and aminoethers. A high ionization potential of aminoethers is possibly unexpected, since substituting a hydrogen or alkyl group at nitrogen by an alkoxy group should not decrease the electron donor ability of nitrogen and thus should not increase the IP. The possible reason for the observed behavior may be the formation of a partial double bond between nitrogen and oxygen in aminoethers. The presence of n-electrons in both nitrogen and oxygen makes this type of bond quite plausible.

Various HALS amines, nitroxides and hydroxylamines (but not aminoethers) have already been studied as quenchers of singlet and triplet states of acetone [33] and anthracene [34] in solution. The results of our experiments show that HALS amines and aminoethers possess completely different properties as donors of electrons and hydrogen atoms. While both HALS amines and aminoethers exhibit similar performances as polymer photostabilizers [35], the results presented in this paper provide evidence for rejecting electron or hydrogen atom transfer as a significant mechanism of HALS polymer photostabilization. Since even BP, being a strong acceptor of electrons and hydrogen atoms relative to peroxy radicals (even acyl peroxy radicals) participating in polymer photo-oxidation, cannot abstract an electron from HALS aminoethers, we conclude that peroxy radicals cannot be involved in an electron or charge transfer process. Therefore the mechanism of in-

teraction of peroxy radicals with HALS aminoethers does not include the stage of an electron or charge transfer and possesses a different nature. We discuss the possible mechanism of peroxy radical–HALS interactions during the polymer photostabilization process in a subsequent paper [36].

Acknowledgments

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